



Hydrogen Behavior in Ion-irradiated Ternary Lithium Oxides

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論 文 内 容 要 旨

Chapter 1

In this chapter, background, purposes and focal points in the present study are described.

The tritium breeding blanket is one of the most important components of a DT fusion reactor because of its direct involvement in both energy extraction and tritium production, both of which are critical to fusion power. As the main objectives for breeding blankets are the simultaneous achievements of: (i) tritium self-sufficiency, (ii) maximised net efficiency (high coolant outlet temperature) and (iii) satisfactory shielding, the required characteristics of the tritium breeding materials are: (a) capable of breeding tritium (Li density), (b) releases tritium, (c) thermal stability and conductivity, and (d) chemical inertness. Lithium-based ceramics (lithium oxide and the ternary ceramics: Li_2O , LiAlO_2 , Li_2TiO_3 , Li_2ZrO_3 and Li_4SiO_4) have been recognized as promising candidates for the tritium breeding materials in the design using solid breeder. Tritium and helium are created as MeV energetic particles owing to the following nuclear reaction between the incident neutron and lithium:



Hydrogen trapping and the processes of damage evolution have been barely understood while the MeV triton loses its energy accompanying formation of the damage along its trajectory and comes to rest within the solid breeder. The present study focuses attention on damage accumulation and hydrogen trapping accompanied by the injection of the energetic hydrogen isotopes and helium ions traveling and coming to rest in ternary lithium oxides.

The purpose in this study is to elucidate the hydrogen trapping and ion-induced damage accumulation, and to examine the interaction between hydrogen and defects in LiAlO_2 , Li_2TiO_3 and Li_2ZrO_3 . For accomplishing the purpose above, the distinguished point in the present study is the directory probing and quantitative evaluation for both of the irradiation damage and the incident ions retained in a solid by means of ion-beam techniques combined with spectrophotometric analysis. Elastic Recoil Detection Analysis (ERDA) was employed to probe hydrogen isotopes within the solid directory and quantitatively. So as to examine the damage accumulation, two

methods were mainly employed: one is in-situ luminescence measurements under ion irradiation, and the other is Rutherford Backscattering Spectroscopy in Channeling geometry (RBS/C) using a single crystalline sample. Luminescence attributed to oxygen vacancies can be observed in the ultraviolet-visible region under ion irradiation in the ternary lithium oxides. The luminescence measurement is a unique technique to allow us to investigate the dynamic process of damage evolution. RBS/C is one of the most powerful techniques to quantitatively determine irradiation damage by probing disorder within a crystalline. For introducing damage and hydrogen, ion irradiation which enables us to perform organized and quantitative investigations is made with hydrogen and helium ions in the energy range from several keV to MeV. The focal points to be elucidated in the present thesis are listed below:

- Dynamic damage process under irradiation of high energy ions (chapter 2)
- Hydrogen trapping during ion implantation (chapter 3)
- Interaction of hydrogen with ion-induced damage (chapter 4)

Interaction varying in the direction along an ion-trajectory between the incident ions and the target atoms is regarded as two regions: the high energy region and the low energy region at the near end of the trajectory. Damage accumulation accompanied by injection of high energy ions is discussed in chapter 2, and hydrogen trapping and damage accumulation near the end of the trajectory of incident hydrogen isotopes are examined in chapter 3 and chapter 4.

Chapter 2:

In this chapter, result and discussion on dynamic damage process accompanied by irradiation of high-energy ion are described.

We focus on the interaction of high-energy ions with atoms in ternary lithium oxides. The dynamic process of damage evolution under irradiation with hydrogen and helium ions in the energy range from several hundred keV to MeV is discussed by means of in-situ luminescence measurements. Here, Li_2ZrO_3 was our focus because of its prominent luminescence under ion irradiation among the ternary lithium oxides. Prior to this discussion on the damage process, optimization of the luminescence measurements was conducted, investigating the characteristics of the luminescence, for example, the luminescent spectra, flux and energy dependence of the intensity. The ion-induced luminescent intensities were proportional to the number of luminescent centers along the trajectory of the incident ions, indicating that the luminescent cross-section was independent of the energy of an incident ion.

The change in the luminescent intensity under irradiation was investigated to examine the production and annihilation processes of luminescent centers attributed to oxygen vacancies. The luminescent intensities monotonically decreased as the fluence of the incident ions increased; the intensities decreased drastically at the beginning of the irradiation, and then, the decreasing rate became smaller with increasing fluence. Decrease in the luminescent intensity during ion irradiation was well explained by a simple phenomenological model involving annihilation and production of the luminescent centers. By evaluating the rate constants of the production and annihilation, it was concluded that the nuclear collisions dominantly contributed to the annihilation and the production

of the luminescent centers under irradiation of high energy protons and helium ions, irrespective of the electronic excitation.

Chapter 3

In this chapter, result and discussion on hydrogen trapping after incident hydrogen loses its energy and comes to rest at the end of the ion trajectory are described.

The focus is on hydrogen trapping after the energetic hydrogen comes to rest due to the energy loss in ternary lithium oxides. In order to elucidate hydrogen trapping, defects and their interaction in the low energy region in Li_2TiO_3 , Li_2ZrO_3 and LiAlO_2 , the depth profile of the hydrogen isotopes retained in the ternary lithium oxides implanted with low energy hydrogen are investigated using ERDA. Their dependences on the fluence, the incident energy, pre-irradiation and the compound were discussed. Besides, a correlation between the defects and hydrogen was discussed by means of the simultaneous measurements of luminescence and ERDA.

Incident hydrogen during implantation was retained only at the near surface depth region, corresponding to the projected range, until the local concentration reached 0.9 H/Ti in Li_2TiO_3 as well as LiAlO_2 . On the contrary, increase of the retained hydrogen was observed at the considerably deeper depth as compared to the projected range in Li_2ZrO_3 . An incident hydrogen is stabilized at the end of its trajectory accompanying lattice relaxation due to chemical interaction with surrounding atoms in Li_2TiO_3 (LiAlO_2), while it can easily migrate from the end of its trajectory via interstitial sites and/or grain boundary in Li_2ZrO_3 . The difference on hydrogen trapping between Li_2TiO_3 (LiAlO_2) and Li_2ZrO_3 is considered to come from the structural characteristics; the migration and detrapping barrier of hydrogen in Li_2ZrO_3 is supposed to be lower than that in Li_2TiO_3 . Simultaneous measurements of ion-induced luminescence and hydrogen concentration revealed that a sample with a higher hydrogen concentration exhibits a lower luminescent intensity. It is speculated that a luminescent center is deactivated by hydrogen trapping.

Chapter 4

In this chapter, result and discussion on damage evolution in the low energy region where a incident hydrogen is trapped, and on the interaction of hydrogen trapping with the damage are described.

The damage accumulation induced by incident energetic hydrogen isotopes was examined near the end of the trajectories, in which the foreign atoms come to rest, i.e., trapping the incident ions which may affect the defect formation in ternary lithium oxides. Here, RBS/C, enabling quantitative discussion on the irradiation damage, is mainly employed using an LiAlO_2 single crystal. Hydrogen isotopes may have a different influence on the defect formation from helium, since the former is expected to have a chemical interaction with defects or target atoms. In addition to the retention and thermal release of hydrogen isotopes, damage accumulation and annealing of defects were investigated to discuss the interaction of the hydrogen trapping with defects induced by ion bombardment via a comparison with helium irradiation.

Damage evolution under irradiation with D and He could be regarded as three stages in an LiAlO_2 single crystal: production of point defects (low fluence), transition into extended defects with an abrupt increase in disorder (middle fluence) and formation of gas bubbles (high fluence). It, however, was found that depth profiles of the ion-induced disorder were quite different between D and He irradiation: the incident D could induce disorder having a depth profile similar to that of the D retained in LiAlO_2 , whereas the depth profile of the disorder induced by He irradiation agreed with that obtained from the calculation based on the binary collision model. In addition to RBS/C, the results of ERDA indicated that an incident D was trapped and might accompany lattice relaxation at the end of its trajectory while an incident He was trapped by vacancies induced by the nuclear collisions accompanied by the ion injection. The lattice relaxation caused by the existence of D results in formation of disorder at the end of the trajectory in the case of D irradiation, which might trap interstitials that diffused due to their concentration gradient from the place where they are created by nuclear collisions. The annealing kinematic of disorder induced by D irradiation also differs from that by He irradiation: the disorder induced by D irradiation to the middle fluence is annealed at a higher temperature (900 K) as compared to that induced by He irradiation (700 K). Besides, increase in disorder is observed even in annealing in the case of D irradiation. This is interpreted as local structural changes with additional distortion due to existence of D contributing to defect growth or change in the local composition. The interaction of D with the defects is supported by the fact that release of D and annealing of the D-induced disorder occur in the same temperature range. Annealing temperature of disorder at a middle fluence was found to be quite higher as compared to a low fluence. The accumulation of several at.% of disorder and hydrogen isotopes retained in LiAlO_2 would cause degradation of release of hydrogen isotopes.

Chapter 5

In this chapter, the conclusions obtained in the present study are described.

In the present thesis, hydrogen trapping and damage evolution accompanied by ion irradiation in ternary lithium oxides (Li_2TiO_3 , Li_2ZrO_3 and LiAlO_2) were examined by means of ion beam analysis techniques combined with spectrophotometric analysis. Dynamic damage process in terms of annihilation and production of luminescent centers attributed to oxygen vacancies under irradiation with high energy hydrogen and helium ions was demonstrated by means of in situ measurements of ion induced luminescence. Hydrogen trapping at the end of the trajectory of the incident hydrogen in Li_2TiO_3 and LiAlO_2 was found to be considerably different from that in Li_2ZrO_3 : incident hydrogen is stabilized at the end of its trajectory accompanying lattice relaxation due to chemical interaction with surrounding atoms in Li_2TiO_3 (LiAlO_2), while it can migrate from the end of its trajectory via interstitial sites and grain boundary in Li_2ZrO_3 . It is revealed that the existence of hydrogen isotopes play a significant role in damage accumulation and structural change due to its chemical interaction during ion irradiation and annealing, in addition to the displacement damage by the nuclear collisions irrespective of species and energy of the incident ions.

論文審査結果の要旨

DT 核融合炉におけるトリチウム固体増殖材の候補として三元系リチウム酸化物が挙げられている。増殖材中の水素同位体挙動および高エネルギー粒子入射にともなう損傷挙動の解明は急務であるにも関わらず、それら挙動評価手法は限られており不明な点が多い。本論文は高速イオンを用いた分析法および分光学的手法を組み合わせることにより三元系リチウム酸化物中の水素捕捉およびイオン照射損傷過程を解明し、またそれらの関係性を検討したものであり、全編 5 章より成る。

第 1 章は緒論であり、DT 核融合炉におけるトリチウム固体増殖材の機能、その候補材として挙げられる各種三元系リチウム酸化物の特性を述べ、水素挙動およびダメージ蓄積挙動解明の重要性を示した。既往研究における問題点を述べるとともに、高速イオンを用いた分析法および分光学的手法を複合的に用いることが最も有効な手段の一つであることを示し、それらを踏まえて本論文の目的と構成を記述した。

第 2 章では、高エネルギーイオン入射にともなう Li_2ZrO_3 中の欠陥形成過程を明らかにするために、高速イオン照射下における酸素欠陥由来のイオン誘起発光をその場測定することにより動的な損傷挙動を調べた。数百 keV から数 MeV の水素およびヘリウムイオン照射下における紫外・可視光領域に観測される誘起発光の入射粒子束密度およびエネルギー依存性等の発光特性を調べ、発光測定の最適化を行った。それに基づき、照射下における発光強度変化を系統的に調べることで、高エネルギーイオン入射にともなう欠陥形成過程は核的はじき出し作用に基づく現象論的モデルを導入することにより説明できることを見出した。

第 3 章では、三元系リチウム酸化物 (Li_2TiO_3 , Li_2ZrO_3 , LiAlO_2) 中の水素捕捉挙動を明らかにするため、反跳粒子検出法を用いて水素イオン注入下における捕捉水素の深さプロファイル変化を調べた。 Li_2TiO_3 および LiAlO_2 中に入射水素は飛跡終端において捕捉され、室温では拡散しないのに対し、 Li_2ZrO_3 では、飛跡終端の捕捉サイトから移動障壁の低いサイトを介して容易に拡散することを明らかにした。また、イオン誘起発光と水素分析の同時測定を行うことで、 Li_2ZrO_3 中の捕捉水素の存在により酸素欠陥の電子状態が変化することを見出し、水素と欠陥の相互作用を示した。

第 4 章では、イオン入射にともなう水素捕捉と欠陥形成の関係を明らかにするために、水素分析および光学的手法に加えて、単結晶 LiAlO_2 を用いた RBS イオンチャネリング法を行うことにより捕捉水素と形成欠陥の双方を系統的に調べた。特に、ヘリウム照射と比較することにより、入射重水素と入射ヘリウムでは欠陥形成過程、熱回復挙動および捕捉、熱放出挙動が異なることを示した。入射重水素は核的はじき出しによる欠陥形成に加え、イオン飛跡終端では重水素捕捉より格子緩和または水素化物の形成が起こることを明らかにし、水素捕捉と欠陥形成が密接に関係することを示した。

第 5 章は統括である。

以上、本論文では本論文は高速イオンを用いた分析法および分光学的手法を組み合わせることにより三元系リチウム酸化物中の水素と欠陥の双方を定量的に調べた一連の研究から、水素捕捉およびイオン入射にともなう損傷過程を明らかにするとともに、それらの関係性を見出すことができた。これらの成果は核融合炉工学の発展に寄与するところが少なくない。

よって、本論文は博士(工学)の学位論文として合格と認める。